
Models for the Description of the H_3O^+ and OH^- Ions in Water

PER E. M. SIEGBAHN

Department of Physics, University of Stockholm, Box 6730, S-113 85 Stockholm, Sweden

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ABSTRACT

Structures of the $\text{H}_3\text{O}^+\text{-OH}^-$ ion pair surrounded by up to three water molecules have been studied. Since the ion-pair structure is always above the corresponding neutral water structure, a constrained geometry optimization is needed. The energy difference between the ion-pair structure and the neutral water structure is studied as a function of the number of surrounding water molecules. The effect of the surrounding water solvent is also studied by placing the model system in a spherical cavity in a dielectric medium. The main results are that the energy difference stabilizes at 10–20 kcal/mol for the larger clusters and that an effect indicating a mechanism for charge separation can be noticed on the geometries of these clusters. Results obtained using gradient-corrected density-functional theory are compared to a configuration interaction treatment using a scaling procedure of the correlation energy. © 1996 by John Wiley & Sons, Inc.

Introduction

Two of the most important reactions occurring in biochemistry and in catalysis, where water is used as solvent, are proton transfer and nucleophilic addition of a hydroxyl anion. The most common quantum chemical approach to the study of these reactions is to simply consider H^+ or OH^- as available from the water solvent and neglect the rest of the solvent. For the nucleophilic addition of a hydroxyl anion to a metal complex in water, the reaction is thus converted into the gas-phase attack of OH^- to the metal complex. An example of a reaction studied in this way¹ occurs in the Wacker process, where the theoretical

progress has recently been reviewed.² The Wacker process is an important technical process where olefins are converted to aldehydes in the presence of a PdCl_2 catalyst. When this nucleophilic addition step was studied again very recently using the highly reliable quantum chemical methods that are now available, it was shown that the gas-phase model works very poorly even as a qualitative model.³ It was, for example, shown that the OH^- attack directly on a coordinated olefin is extremely exothermic by 101 kcal/mol, which is a totally unrealistic result. The model was also shown to be qualitatively incorrect for answering the important question of where the olefin attacks—on the metal center or on the olefin. This question has been addressed by experiments, and detailed information has been obtained based on stereochemical

arguments.^{4,5} It is thus known from experiments that it is the hydroxyl attack on the olefin that proceeds further to form the aldehyde in the Wacker process. However, the indications from experiments are that the energetically preferred attack is probably on the metal center, but from this point there will be no migration toward the olefin. In contrast to the conclusions drawn from experiments, the calculations on the gas-phase model for an OH^- attack give the result that the OH^- attack on the olefin is preferred by as much as 43 kcal/mol.³ The true result for the reaction in water is most likely a preference by 10–20 kcal/mol for the attack on the other site—on the metal center. The gas-phase model thus also appears to be totally unreliable for this relative energy difference. Overall, it is clear from these recent calculations that a quite different model is needed to treat the nucleophilic addition.

In an attempt to improve the above gas-phase model for the Wacker process, effects of the water solvent were incorporated in a recent model study.⁶ The simplest approach to study the qualitative effects of a solvent is to introduce a reaction field by using the self-consistent reaction field (SCRF) theory.⁷ In this theory the molecule which is explicitly studied is put in a spherical cavity surrounded by a dielectric medium. However, it was shown in ref. 6 that this model is far too crude for the nucleophilic addition reaction. The very large exothermicity of the OH^- attack was reduced from 101 kcal/mol (see above), but only down to 75 kcal/mol. The unrealistic energy difference between the two sites of attack of 43 kcal/mol was hardly modified at all (only by 3 kcal/mol) by the presence of the reaction field. In order to get a more realistic energy difference for the two sites of attack, it was furthermore shown in ref. 6 that an explicit treatment of the positive counterion—in this case H_3O^+ —is required. When H_3O^+ is added to the gas-phase model, the attack on the metal center was actually found to be preferred, in line with the experimental indications. The energy difference between the two sites of attack was found to be 12 kcal/mol.

In the recent general study of several steps of the Wacker process,³ another indication of a problem with a simple gas-phase model was also found. At a later stage of the process, an O-H bond of a hydroxyethyl ligand has to be broken. The mechanism believed to be involved was a β -type elimination. However, the high accuracy calculations showed that the barrier for this step in the gas phase is far too high. The alternative mechanism

suggested was a proton transfer from the hydroxyethyl group mediated by direct involvement of water molecules in the solvent. This hypothesis was drawn basically because it is hard to imagine any other mechanism. No calculations to test this suggestion were made since there is no available model for describing proton transfer in a realistic way.

The above examples taken from the Wacker process show that more useful quantum chemical models to describe the very common reactions of proton transfer and nucleophilic addition are badly needed. The present study represents the start of a development of such models. It is clear that a key reaction in this context is the dissociation of water into H_3O^+ and OH^- , and there does not seem to be any previous quantum chemical study of this dissociation. In contrast, there are several similar studies of proton transfer in water,^{8,9} which is also a difficult reaction to model but still very much simpler than the dissociation of water. A major complication in the present context is that the formation of H_3O^+ and OH^- does not represent a stable minimum. Based on the dissociation constant of water, the free energy of the $\text{H}_3\text{O}^+\text{-OH}^-$ pair should be 24 kcal/mol higher than the energy of two H_2O . This estimate also includes temperature-dependent effects. In the present study, the main question addressed is how many hydrogen-bonded water molecules are needed to stabilize the $\text{H}_3\text{O}^+\text{-OH}^-$ pair reasonably well. In order to attack this problem, the energy for the fully geometry-optimized structure of up to five water molecules is compared to the energy obtained for a structure where the geometry of one H_3O^+ is constrained with fixed O-H distances. The latter constraint is needed since the $\text{H}_3\text{O}^+\text{-OH}^-$ pair is not stable otherwise. These structures were placed in a cavity of a dielectric medium using SCRF theory. Results obtained using recently developed density-functional theory (DFT) methods¹⁰ and the parametrized configuration interaction with parameter 80 (PCI-80) method¹¹ are compared. In this context it is of interest to know that different DFT methods have recently been used by Suhai¹² in an extensive study of water polymers ranging from the dimer to the infinite chain.

Computational Details

In the calculations reported in the present paper on water clusters, basis sets of double zeta plus

polarization quality have been used. Both DFT and PCI-80 calculations have been performed to obtain the final energies. The structures were optimized at the DFT level without polarization functions.

In most of the comparisons done below the energies were obtained at the DFT level. The three-parameter Becke functional¹⁰ (B3LYP) as implemented in GAUSSIAN92/DFT¹³ was used. Some comparative calculations at the PCI-80 level¹¹ were also performed. In this scheme which was recently developed, the underlying correlated calculations are done at the modified coupled-pair functional¹⁴ (MCPF) level using the STOCKHOLM set of programs.¹⁵ Even though the absolute accuracy of the MCPF calculations is not very high, the fact that the errors are highly systematic can be used to significantly reduce the relative errors. Based on comparisons to calculations of high accuracy and on comparisons to experiments, it has recently been demonstrated that the present type of treatment gives a remarkably stable fraction of the correlation effects, which is close to 80% using the present basis sets. A simple estimate of the remaining correlation effects is then obtained by simply adding 20% correlation energy to each system. For a benchmark test, consisting of the atomization energies of 32 neutral first row systems, the PCI-80 scheme gives an average absolute deviation compared to experiments of only 2.4 kcal/mol.¹¹ A similar high accuracy on the same benchmark is obtained using the B3LYP version of DFT, and comparisons of the results obtained at these quite accurate levels will be made below. It is interesting to note that the philosophy in the two approaches is quite similar with use of a limited number of (one for PCI-80 and three for B3LYP) empirical parameters.

The basis set used for oxygen is the primitive (9s,5p) basis of Huzinaga¹⁶, contracted to double zeta. For the energy evaluation one *d* function with exponent 0.85 was added in the DFT calculations and one with exponent 1.0 was used for the PCI-80 calculations. For hydrogen a primitive (4s) basis¹⁷ was used contracted to double zeta, and for the energy evaluation one *p* function with exponent 1.0 was added in the DFT calculations. For the PCI-80 calculations a primitive 5s basis contracted to three functions and a *p* exponent of 0.8 were used.

Two types of geometry optimization were performed in the present investigation. In the first type, performed for the neutral water structures, all geometric parameters were fully relaxed. If this type of geometry optimization is performed for the

ion-pair structures, the geometry will collapse to the corresponding water structure, since this type of structure is always lower in energy. In order to prevent this collapse, the O-H bond distances in H₃O⁺ were kept at fixed values. The O-H bond pointing toward OH⁻ was frozen at 1.04 Å, while the other two O-H distances were kept at 1.00 Å. The energies should be very insensitive to the precise values chosen for these distances. All other degrees of freedom were optimized in the ion-pair structures. The level of geometry optimization was tested for free H₃O⁺ without constraints by adding polarization functions in this step. This only led to an energy improvement in the fifth decimal place for the final B3LYP energy, but could be more important for the systems where H₃O⁺ becomes pyramidal. The use of double zeta basis sets in the geometry optimization was, anyway, considered sufficient for the present qualitative purposes. At each optimized geometry the Hessian was computed from which zero-point vibrational effects as well as temperature-dependent thermodynamic information were obtained following standard textbook procedures. The temperature used was 298.15 K. These calculations were done at the B3LYP level with the above-described double zeta basis sets using GAUSSIAN92/DFT.

In order to account for the effects of the surrounding solvent, SCRF calculations⁷ were finally performed using GAUSSIAN92/DFT. The dielectric constant of water was taken to be 80.4. The cavity radii were obtained following the standard procedure in the program. The volume inside a contour of 0.001 electrons/bohr³ density was first determined. The radius of the spherical cavity is then taken to be 0.5 Å larger than the radius corresponding to this volume.

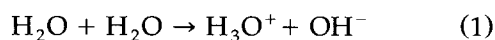
Results and Discussion

The present discussion is divided into four subsections. In the first subsection the H₃O⁺-OH⁻ pair is compared to the H₂O dimer. For the ion pair, the O-H distances of H₃O⁺ are constrained to be 1.04 Å for the bond pointing toward OH⁻ and to be 1.00 Å for the other two bonds. No constraint was put on the O-H distance in OH⁻. The geometry of the water dimer was varied freely. In the second subsection, another water molecule is added and the same type of calculations were repeated with the same geometry constraint for H₃O⁺. In the third subsection, still another water

molecule is added and, finally, in the fourth subsection, all together five water molecules are treated. DFT and PCI-80 results are discussed with and without dielectric reaction fields added. Temperature-dependent effects are also briefly discussed. The energetic results are summarized in Table I. In Table II the reaction field effects are given and, finally, in Table III charges from the Mulliken population analysis are given.

(H₂O)₂ AND THE H₃O⁺-OH⁻ PAIR

Before the results of the water dimer are discussed, a few comments can be made on the results for the isolated ions and molecules. The gas-phase dissociation of water into ions,



is endothermic by as much as 222.4 kcal/mol (B3LYP). Placing the ions in a spherical cavity in a dielectric medium will obviously decrease the endothermicity mainly by charge polarization of the medium. The charge polarization energy dependence of the solvation energy is given by

$$E = \frac{\epsilon - 1}{2\epsilon} \frac{q^2}{R} \quad (2)$$

where R is the cavity radius and ϵ is the dielectric constant. With a cavity radius (see Computational Details) of 2.47 Å for H₃O⁺ and one of 2.63 Å for OH⁻, the charge polarization effect is 124.3 kcal/mol. Other effects of the dielectric medium depending on the dipole moments of the ions and molecules actually lead to a small increase of the endothermicity by 6.3 kcal/mol. All together, the effect of the dielectric medium is to reduce the

endothermicity from 222.4 down to 104.4 kcal/mol. Even if this effect is large, it is not at all enough to bring the endothermicity down to reasonable values (see Introduction). The major effect missing is the electrostatic attraction between H₃O⁺ and OH⁻, which is neglected in this approach where the isolated ions are considered. To circumvent this problem, the two ions are therefore studied together as an ion pair in the following. An alternative approach would be to decrease the cavity radii substantially, but this would probably lead to other artificial problems.

The structure obtained for the constrained optimization of the H₃O⁺-OH⁻ pair is shown in Figure 1. The corresponding water dimer equilibrium is quite similar, but with the relevant O-H distances lengthened and shortened, respectively, and is therefore not shown in a figure. The hydrogen bonding O-H distance in the water dimer is 1.75 Å, but is considerably shorter—only 1.17 Å—for the H₃O⁺-OH⁻ pair. The binding energy (including zero-point vibration) for the water dimer is 3.5 kcal/mol at the B3LYP level and 3.3 kcal/mol at the PCI-80 level. The B3LYP energy difference between the two structures is 42.9 kcal/mol, in good agreement with the PCI-80 value of 45.3 kcal/mol. Adding temperature-dependent effects from the enthalpy and from the entropy leads to a slightly higher value of 43.7 kcal/mol (B3LYP). These effects go in the expected direction with a higher entropy for the water dimer than for the ion pair and with a higher vibrational enthalpy also for the dimer. The energy difference of 43.7 kcal/mol is much higher than the free-energy difference of 24 kcal/mol in water (see Introduction). This overestimate of the energy difference for the isolated water dimer is an expected result since the sur-

TABLE I.
Results of the Calculations on the H₃O⁺-OH⁻(H₂O)_{*n*} Systems.

<i>n</i>	O ⁻ -H	ΔE_0	$\Delta E(T)$	$\Delta E(\text{SCRF})$	$\Delta E(n+2)$
0	1.17	42.9 (45.3)	43.7	-12.8	3.5 (3.3)
1	1.30	28.8 (32.0)	30.0	-3.0	12.8 (10.1)
2 ^a	1.34	24.2 (21.4)	25.4	-8.7	16.5 (13.7)
2 ^b	1.30	20.5 (22.3)	21.2	-1.6	23.5 (17.4)
3	1.34	16.2 (18.6)	17.9	-8.9	27.9 (22.2)

Energies (kcal/mol) are given with respect to the H₂O)_{*n*+2} systems and were obtained at the B3LYP level including zero-point vibrational effects. Energies in parentheses are at the PCI-80 level. ΔE_0 is the gas-phase energy difference, $\Delta E(T)$ also includes temperature-dependent effects, and $\Delta E(\text{SCRF})$ is the contribution from the dielectric reaction field. $\Delta E(n+2)$ is the binding energy of *n* + 2 water molecules. O⁻-H (Å) is the hydrogen-bond distance between OH⁻ and H₃O⁺.

^a Structure in Fig. 3.

^b Structure in Fig. 4.

TABLE II.
Reaction Field Effects [$\Delta E(\text{SCRF})$] for the
Energy Difference between H₃O⁺-OH⁻ (H₂O)_n and
(H₂O)_{n+2}, Obtained at the B3LYP Level (kcal/mol).

<i>n</i>	μ	<i>R</i>	$\Delta E(\text{SCRF})$
0	5.83	3.02	-12.8
1	2.71	3.33	-3.0
2 ^a	6.63	3.72	-8.7
2 ^b	2.31	3.75	-1.6
3	6.43	3.84	-8.9

μ is the dipole moment (D) and *R* is the radius (Å) of the spherical cavity in the dielectric medium.

^a Structure in Fig. 3.

^b Structure in Fig. 4.

rounding water should stabilize an ionic structure much more than the hydrogen-bonded structure. If the surrounding solvent has dielectric constant ϵ , a molecule with radius *R* and dipole moment μ gives a polarization energy *E* of the solvent, which is expressed as

$$E = \frac{\epsilon - 1}{2\epsilon + 1} \frac{\mu^2}{R^3} \quad (3)$$

The dipole moment of the H₃O⁺-OH⁻ is found to be 5.83 D; for the water dimer it is smaller (3.71 D). The cavity radii of the two systems are almost the same (3.0 Å) and the dielectric constant of water is 80.4. With these values, the polarization energy difference between the two systems can be estimated to be about 5.3 kcal/mol. The actually calculated polarization energy difference obtained at the B3LYP level by putting the systems in the dielectric medium is 6.8 kcal/mol. In the DFT calculation the electronic relaxation effect on the water dimer and the ion pair due to the induced dipole field of the surrounding medium is also obtained. This effect also favors the ion pair; the B3LYP difference is 6.0 kcal/mol. All together, these two effects thus favor the ion pair by 12.8

kcal/mol, bringing the gas-phase difference down from 43.7 kcal/mol to 30.9 kcal/mol. Since the correct energy difference should be about 24 kcal/mol, it is clear that the treatment of the surrounding water as a dielectric medium is too simplified. Explicit consideration of additional water molecules is thus needed and will be discussed in subsequent subsections.

(H₂O)₃ AND THE (H₃O⁺-OH⁻)(H₂O) SYSTEM

When a water molecule is added to the H₃O⁺-OH⁻ pair the structure obtained in Figure 2 is obtained in the constrained-geometry optimization. This is a quite symmetric triangular-type structure where the added water molecule stabilizes both H₃O⁺ and OH⁻ by hydrogen bonding. Through this stabilization the hydrogen bond between H₃O⁺ and OH⁻ is lengthened from 1.17 Å in the free ion pair in Figure 1 to 1.30 Å in the structure in Figure 2. The hydrogen bonds to the water molecule are rather short, significantly shorter than the one in the water dimer. The O-H hydrogen bond between water and H₃O⁺ is 1.51 Å and the one between water and OH⁻ is 1.41 Å. The corresponding water trimer structure is similar to the one in Figure 2 and is not shown. For the trimer, the three O-H hydrogen-bond distances are 1.67–1.69 Å, somewhat shorter than for the dimer where it is 1.75 Å. The binding energy of the trimer is 12.8 kcal/mol at the B3LYP level. The PCI-80 value is somewhat smaller (10.1 kcal/mol), indicating overall slightly weaker hydrogen bonds at this level. The trimer binding energy is very close to three times the energy for the water dimer, in line with the fact that there are three hydrogen bonds. This value is also in the range of results obtained recently at different high levels of treatment by Fowler and Schaefer.¹⁸

The energy difference between the trimer and the ion-pair structure in Figure 2 is 28.8 kcal/mol (PCI-80: 32.0 kcal/mol), which is significantly lower

TABLE III.
Charges for the H₃O⁺-OH⁻ (H₂O)_n Ion-Pair Systems Obtained at the B3LYP Level.

<i>n</i>	H ₃ O ⁺	OH ⁻	H ₂ O	H ₂ O	H ₂ O
0	+0.59	-0.59			
1	+0.59	-0.54	-0.05		
2 ^a	+0.56	-0.56	+0.07	-0.07	
2 ^b	+0.59	-0.52	-0.02	-0.05	
3	+0.57	-0.52	+0.07	-0.04	-0.07

^a Structure in Fig. 3.

^b Structure in Fig. 4.

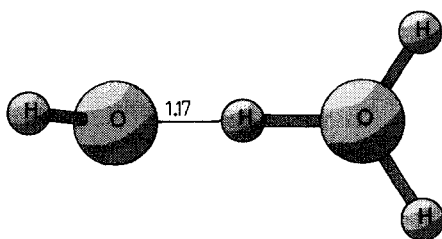


FIGURE 1. The geometry-optimized structure for the $\text{H}_3\text{O}^+\text{-OH}^-$ ion pair.

than the difference of 42.9 kcal/mol found without the third water. Temperature effects increase the energy difference to 30.0 kcal/mol (B3LYP). Since the water molecules are organized so symmetrically (see Fig. 2), the total dipole moment is small. For the water trimer it is only 0.71 D and for the ion pair it is 3.02 D. This gives a rather small absolute stabilizing effect when the systems are placed in a dielectric medium and the relative stabilization of the ion pair is only 3.0 kcal/mol. A final energy difference between the two structures is then 27.0 kcal/mol, which is not far away from the difference of 30.3 kcal/mol found for the dimer and of 24 kcal/mol from the experimental water result. The rather large direct stabilization found by adding the third water molecule is thus partly canceled by a smaller dielectric medium effect. This could indicate a certain convergence of the model, but is actually somewhat accidental, see subsequent text.

$(\text{H}_2\text{O})_4$ AND THE $(\text{H}_3\text{O}^+\text{-OH}^-)(\text{H}_2\text{O})_2$ SYSTEM

After the first water molecule has been added to the $\text{H}_3\text{O}^+\text{-OH}^-$ ion pair, there are two natural places where the next water molecule could be placed: Either the water molecule could be placed

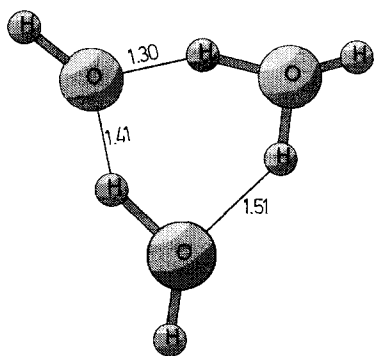


FIGURE 2. The geometry-optimized structure for the $\text{H}_3\text{O}^+\text{-OH}^-(\text{H}_2\text{O})$ system.

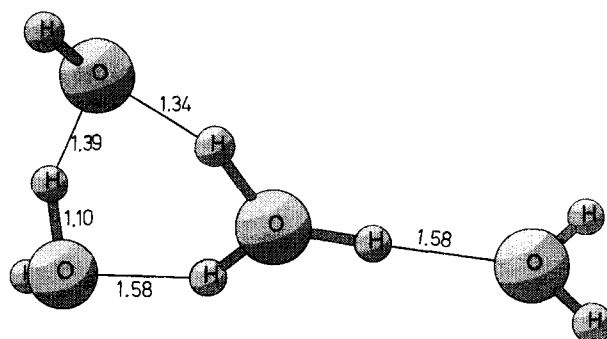


FIGURE 3. The first (see text) geometry-optimized structure for the $\text{H}_3\text{O}^+\text{-OH}^-(\text{H}_2\text{O})_2$ system.

to hydrogen-bond to the remaining O-H bond in H_3O^+ or it could be placed to hydrogen-bond to the O-H bond in OH^- . In the present subsection these two different structures will be discussed. Adding a second water molecule attached to H_3O^+ leads to the optimal structure shown in Figure 3. One sign of the increased stabilization obtained by adding this water is seen for the hydrogen-bond distance between H_3O^+ and OH^- , which is increased from 1.30 Å with one water molecule to 1.34 Å with two water molecules added. Another sign of the increased stability is that the two hydrogen-bond distances to OH^- are now approaching each other. With one water molecule added, these O-H distances were 1.30 and 1.41 Å; with two water molecules added, they are 1.34 and 1.39 Å. The two other hydrogen bonds in Figure 3 are 1.58 Å. This distance is longer than with one water (1.51 Å) and is approaching the distance for the water tetramer where these distances are 1.68–1.83 Å. The binding energy of the tetramer is 16.5 kcal/mol (B3LYP), which is 3.7 kcal/mol more than for the trimer and is in line with the single additional hydrogen bond formed.

With the addition of the second water molecule attached to H_3O^+ , the energy difference between the ion pair and the water structure continues to decrease, from 28.8 kcal/mol with one water molecule to 24.2 kcal/mol with two water molecules added. Temperature effects increase this value to 25.4 kcal/mol. Since the tetramer structure in Figure 3 is much less symmetric than the trimer structure in Figure 2, the dipole moment is much larger for the tetramer. For the tetramer the dipole moment is 4.26 D and for the ion pair in Figure 3 it is as large as 6.63 D. This leads to a substantial stabilization of 8.7 kcal/mol of the ion-pair structure compared to the tetramer structure by the dielectric medium. The final energy

difference between the structures is thus 16.7 kcal/mol, which is about 10 kcal/mol lower than for the trimer. Thus, in this case the reaction field effects are less successful in stabilizing the energy difference between the two structures to the experimentally observed difference of 24 kcal/mol. A problem with the structure shown in Figure 3, which should finally be mentioned, is that this structure is not a true minimum for the water tetramer. The computed Hessian has one imaginary frequency of 238 cm⁻¹.

The second possible structure for (H₃O⁺·OH⁻)(H₂O)₂ is obtained by placing the second water molecule to hydrogen-bond to the O-H bond in OH⁻. However, when one more water molecule is added at this place, the expected structure is not obtained after the constrained geometry optimization. Instead, the quadratic structure shown in Figure 4 is found, with the added water molecules added previously. For this structure the water tetramer is in a true minimum with no imaginary frequency of the Hessian. The structure in Figure 4 has one particularly interesting feature. The bond distance for the O-H bond of the water molecule pointing toward OH⁻ is now as long as 1.14 Å. With only one water molecule added, this bond was 1.09 Å. This bond is thus approaching the length of the hydrogen bond for the same hydrogen to OH⁻, which is now 1.29 Å; with one water molecule it was 1.41 Å. This effect becomes even more pronounced when still another water is added; see the next subsection.

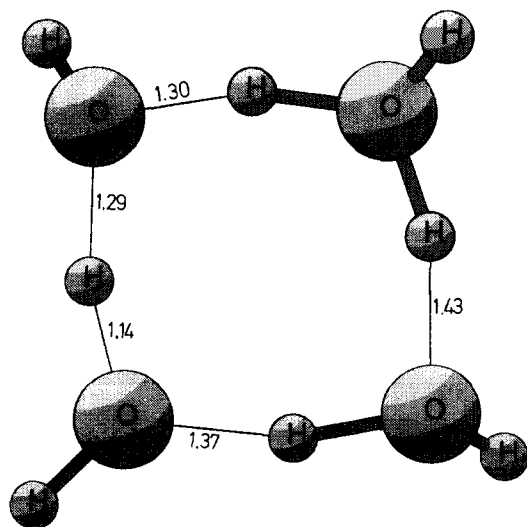


FIGURE 4. The second (see text) geometry-optimized structure for the H₃O⁺·OH⁻(H₂O)₂ system.

The quadratic structure of the water tetramer as in Figure 4 is significantly lower in energy than the structure in Figure 3 for both the ion-pair and the neutral system. The binding energy of the quadratic neutral tetramer is 23.5 kcal/mol (B3LYP), which is as much as 7.0 kcal/mol more than for the tetramer structure in Figure 3. This effect is not as pronounced, but still present, at the PCI-80 level, where the increased stability is 3.7 kcal/mol and the total binding energy is 17.4 kcal/mol. It should be added that this quadratic tetramer may still not be the lowest point on the potential surface, but is the local minimum which is closest to the ion-pair structure in Figure 4. Any comparison to an optimal tetramer structure of a different topology than the one selected for the ion pair is not relevant for the present study.

The energy difference between the ion-pair and the neutral system for the quadratic structure is 20.5 kcal/mol (B3LYP), which is 3.7 kcal/mol less than for the other structure. At the PCI-80 level the energy difference for the quadratic structure is 22.3 kcal/mol. Temperature effects lead to an energy difference of 21.2 kcal/mol (B3LYP). Since the quadratic structure is more symmetric than the other structure, the dipole moment is smaller and, therefore, also the dielectric medium effect. For the quadratic structure the relative energy lowering of the ion-pair system is thus only 1.6 kcal/mol, which leads to a final energy difference between the two systems of 19.6 kcal/mol. This is smaller than the experimental energy difference of 24 kcal/mol, but similar to the 16.7 kcal/mol found for the other tetramer structure.

(H₂O)₅ AND THE (H₃O⁺·OH⁻)(H₂O)₃ SYSTEM

When still another water molecule should be added to form a pentamer system, it was decided to start from the lowest energy tetramer, the quadratic structure in Figure 4, and attach this water molecule to the remaining O-H bond in H₃O⁺. This leads to the structure shown in Figure 5 for the ion pair after the constrained-geometry optimization. For the water pentamer this is a true minimum without any imaginary frequencies of the Hessian. The most interesting aspect of this geometry occurs for the bonding between OH⁻ and the water molecule attached to it. The bond distance for the O-H bond of the water molecule that points toward OH⁻ has now increased from 1.14 to 1.17 Å for the tetramer. Since the hydrogen bond distance for the same hydrogen to OH⁻

simultaneously has decreased from 1.29 down to 1.26 Å, these two O-H bond distances are now quite close and the hydrogen atom is thus not far from the midpoint between the two oxygen atoms. It is clear that a situation is building up where a proton can start to move toward the original OH^- from a previous water molecule to create a new OH^- and thereby increase the distance between the ions in the ion pair. This mechanism with a proton moving rather than one where the H_3O^+ and OH^- ions move as entities, appears to be a likely mechanism for charge separation in water. Another interesting structural parameter is the hydrogen-bond distance between OH^- and H_3O^+ , which for the system in Figure 5 is 1.34 Å. From the results for the smaller clusters (see Table I) it appears that this bond distance is close to converged at this value. The other hydrogen-bond distances for the ion-pair pentamer are in the range 1.34–1.47 Å for the bonds in the square and it is 1.60 Å to the fifth water outside the square. For the neutral pentamer they are in the range 1.45–1.60 Å in the square and 1.72 Å to the fifth water.

The energy difference between the ion-pair and the neutral pentamer system is 16.2 kcal/mol compared to 20.5 kcal/mol for the tetramer. The PCI-80 value for the pentamer is 18.6 kcal/mol. With temperature-dependent effects added, the difference is 17.9 kcal/mol (B3LYP). The energy difference thus continues to go down with the number of added water molecules and is not converged yet even though a certain stabilization around 20

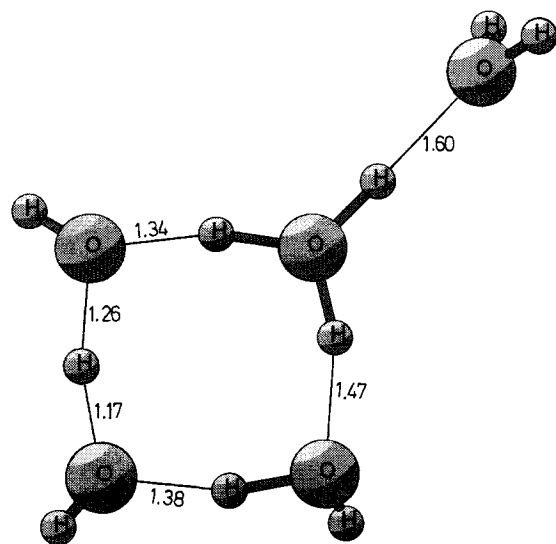


FIGURE 5. The geometry-optimized structure for the $\text{H}_3\text{O}^+ - \text{OH}^- (\text{H}_2\text{O})_3$ system.

kcal/mol can be observed. However, when the reaction field is added, there is no longer such stabilization. When a water molecule is added to the quadratic tetramer structure in Figure 4 to form the ion-pair pentamer structure in Figure 5 there is a major change of dipole moment from 2.31 to 6.43 D. This means that the reaction field effect will also be much larger for the pentamer; that is, 8.9 kcal/mol compared to 1.6 kcal/mol for the tetramer. It is also interesting to note that the cavity radii are about the same for the two systems; see Table II. It is likely that the procedure of placing a system in a spherical cavity works better the more spherical the system is. Therefore, the dielectric effect will be somewhat exaggerated for the pentamer system in Figure 5 since it is more spread out in two dimensions. If the overall results in Table I of adding the reaction field are summarized, there are no clear indications that the addition of these effects in this way actually leads to an improved convergence of the relative ion-pair stability.

The reason for the low dipole moment of the tetramer in Figure 4 is that the orientations of the individual water dipoles are opposite to each other and will thus have a canceling effect on the total dipole moment. A similar effect is seen for the symmetric trimer in Figure 2. When the fifth water molecule is added to the tetramer, this water molecule will not have any corresponding water oriented in the opposite direction. Also, the fifth water molecule has a stabilizing effect on H_3O^+ since it is attached to this ion. The charge on H_3O^+ in the tetramer in Figure 4 is +0.57; see Table III. The sum of the charges on H_3O^+ and the attached water in Figure 5 is +0.64. As a general comment, it appears that the dipole moments of the clusters chosen as models must, to some extent, vary in a random way and, for this reason, it will be difficult to obtain cluster size convergence for the dielectric field effect. The symmetric models with a low dipole moment seem in certain aspects to be better models than the less symmetric models, but this conclusion can be debated.

Conclusions

A set of small molecular models of the ion pair $\text{H}_3\text{O}^+ - \text{OH}^-$ surrounded by water molecules has been studied. This was done as an initial step toward development of realistic models for the

important reactions of proton transfer and nucleophilic addition in water. At present, even qualitatively reasonable models for these reactions are lacking. The present results show that a reasonable degree of stability already is obtained for the H₃O⁺ – OH⁻ ion pair after addition of a few surrounding water molecules. In the gas-phase models, the energy difference between the ion-pair and the neutral water system is stabilized from about 40 kcal/mol without any surrounding water molecules to about 20 kcal/mol when three water molecules are added. When the systems are placed in a spherical cavity in a dielectric medium, the effects of the surrounding solvent can be estimated by SCRF theory. These effects depend strongly on the dipole moment of the molecular model, and a convergence of the effects is therefore not obtained. The results vary in the range 2–9 kcal/mol relative energy lowering for the ion pair for the clusters with three to five water molecules. In fact, for the systems studied, the addition of the SCRF effects did not help to stabilize the relative ion-pair stability. The relative stability of 20 kcal/mol obtained without the reaction field effects for the larger clusters is in quite reasonable agreement with the free energy difference of 24 kcal/mol, which can be estimated from real water. It should be added that to obtain a precise value for this energy difference is obviously not the purpose of the present study. Instead, conclusions that can be drawn relate to the size of the models that have to be used to model reactions in water and the level of accuracy that can be obtained.

One of the most interesting results of the present study appeared for the quadratic structure of the tetramer and for the corresponding pentamer. For the pentamer the constrained-geometry optimization led to a structure where one of the hydrogen atoms is close to the midpoint between OH⁻ and a water molecule. With only a slight displacement of this proton, the OH⁻ would be turned into a water molecule and a water molecule would be turned into an OH⁻. This leads to an effective substantial increase of the separation between the ions of the H₃O⁺-OH⁻ ion pair and appears to be a likely mechanism for ion motion in real water.

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